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Determination of Natural and Depleted Uranium in Urine at the ppt Level: An Interlaboratory Analytical Exercise

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Technical Report
DRDC Suffield TR 2002-024
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Canada

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Abstract

An analytical exercise was initiated in order to determine those analytical procedures with the capacity to measure uranium isotope ratios ($^{238}U/^{235}U$) in urine samples containing less that 1 µg uranium /L urine. A host laboratory was tasked with the preparation of six sets (12 samples per set) of synthetic urine samples spiked with varying amounts of natural and depleted (0.2% ^{235}U) uranium. The sets of samples contained total uranium in the range 25 ng U/L urine to 770 ng U/L urine, with isotope ratios ($^{238}U/^{235}U$) from 137.9 (natural uranium) to 215 (~50% depleted uranium). Sets of samples were shipped to five testing laboratories (four Canadian and one European) for total and isotopic assay. The techniques employed in the analyses included sector field inductively coupled plasma mass spectrometry (ICP-SF-MS), quadrupole inductively coupled plasma mass spectrometry (ICP-Q-MS), thermal ionization mass spectrometry (TIMS) and neutron activation analysis (NAA). Full results were obtained from three testing labs (ICP-SF-MS, ICP-Q-MS and TIMS). Their results, plus partial results from the NAA lab, have been included in this report. Total uranium and isotope ratio results obtained from ICP-SF-MS and ICP-Q-MS were in good agreement with the host lab values. Neutron activation analysis and TIMS reported total uranium concentrations that differed from the host lab. An incomplete set of isotopic ratios was obtained from the NAA lab with some results reporting enriched uranium (%$^{235}U > 0.7$). Based on the reported results, the four analytical procedures were ranked: ICP-SF-MS (1), ICP-Q-MS (2), TIMS (3) and NAA (4).

Résumé

Un exercice analytique a été initié dans le but de déterminer les procédures analytiques qui ont la capacité de mesurer les taux isotopiques d'uranium ($^{238}U/^{235}U$) dans des échantillons d'urine contenant moins d'1 µg d'uranium /L d'urine. Un laboratoire hôte a eu pour mission de préparer six ensembles (12 par ensemble) d'échantillons d'urine synthétique, ensemencés de quantités différentes d'uranium naturel et appauvri (0.2% ^{235}U). Les ensembles d'uranium contenaient une quantité totale d'uranium allant de 25 ng d'U/L d'urine à 770 ng d'U/L, avec des taux isotopiques ($^{238}U/^{235}U$) allant de 137.9 (uranium naturel) à 215 (~50% d'uranium appauvri). Des ensembles d'échantillons ont été envoyés dans cinq laboratoires d'essais (quatre canadiens et un européen) pour des mesures des quantités totales d'uranium et des isotopes. Les techniques employées dans les analyses comprenaient la spectrométrie de masse à plasma inductif à haute résolution (ICP-SF-MS), la spectrométrie de masse quadripolaire à plasma inductif (ICP-Q-MS) la spectrométrie de masse à ionisation thermique (TIMS) et l'analyse par activation neutronique (NAA). Des résultats complets ont été obtenus de trois laboratoires d'essais (ICP-SF-MS, ICP-Q-MS et TIMS). Leurs résultats, avec ceux plus partiaux du laboratoire de NAA ont été inclus dans ce rapport. Les rapports isotopiques et d'uranium total obtenus à partir de ICP-SF-MS et ICP-Q-MS correspondaient bien à ceux des valeurs obtenues par le laboratoire hôte. L'analyse par activation neutronique et TIMS enregistraient des concentrations d'uranium total qui différaient de celles du laboratoire hôte. Le laboratoire de NAA a produit un ensemble incomplet de taux isotopiques avec quelques résultats signalant un uranium enrichi : (%$^{235}U > 0.7$). Les quatre procédures analytiques ont été classées selon les résultats enregistrés: ICP-SF-MS (1), ICP-Q-MS (2), TIMS (3) et NAA (4).

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Executive summary

Introduction: The Canadian Forces (CF) may be called on to perform peacekeeping or battlefield operations in regions of the world where there is a significant threat of exposure to environmental hazards. To operate effectively in these theatres the CF must be able to identify the hazard, take steps to minimize exposure and provide follow up analyses. Recent concern has arisen over the possibility of past exposure to depleted uranium following the Gulf War and the Kosovo conflict. This has led to the establishment of a CF voluntary uranium bioassay program. To date, two hundred active and retired members of the CF have submitted urine samples for total uranium assay and over eighty have submitted hair samples for isotope ratio ($^{238}U/^{235}U$) analysis. Test results, to date, have been negative for the presence of depleted uranium, but questions have arisen about the sensitivity of analytical methods employed.

The purpose of this analytical exercise was to evaluate all available analytical techniques with the capability to measure uranium isotope ratios ($^{238}U/^{235}U$) at trace concentrations (sub-parts per billion) in biological fluids (e.g., urine). Synthetic urine was chosen in this study to negate any concern over biohazards. The techniques chosen for this study included sector field inductively coupled plasma mass spectrometry (ICP-SF-MS), quadrupole inductively coupled plasma mass spectrometry (ICP-Q-MS), thermal ionization mass spectrometry (TIMS) and neutron activation analysis (NAA).

Results: Sets of 12 samples (2 blanks and 10 samples doped with varying amounts of natural and depleted uranium) were prepared by the host laboratory and shipped to five independent testing laboratories for total uranium and isotope ratio assays. Two MS laboratories (sector field and quadrupole ICP-MS) submitted total uranium and isotope ratio measurements that were in good agreement with the host laboratory's values. Total uranium values from TIMS and NAA deviated from the host values. Both techniques overestimated total uranium at low concentrations and underestimated it at high concentrations. The high precision in the TIMS isotope ration measurements was negated by problems with the accuracy of the measurements. The partial set of isotope ratio measurements from NAA were the least accurate with $^{238}U/^{235}U$ ratios indicative of enriched uranium ($^{235}U > 0.72\%$).

Significance: Neutron activation analysis (NAA) was shown to not be suitable for total and isotopic uranium bioassays. Mass spectrometry techniques (ICP-Q-MS, ICP-SF-MS and TIMS) were shown to be more precise and have lower detection limits (total and isotope ratios) when compared to NAA.

Future Plans: A second study with real urine samples could be considered. The total uranium in >99% of the urine samples analysed by the current CF testing program were below the concentration of uranium (25 ng U/L synthetic urine) in the synthetic blanks. The second study could include natural urine samples with total uranium in the range of 1 ng U/L urine to 100 ng U/L urine. All three MS (ICP-SF-MS, ICP-Q-MS and TIMS) techniques were found to be suitable for a follow up study

D'Agostino, P.A., Ough, E.A., Glover, S.E. and Vallerand, A.L., 2002. Determination of Natural and Depleted Uranium in Urine at the ppt Level: An Interlaboratory Analytical Exercise. DRDC Suffield TR 2002-024. DRDC Suffield.

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Sommaire

Introduction: Les Forces canadiennes (FC) peuvent être appelées à effectuer des opérations de maintien de la paix ou de champ de bataille dans des régions du monde où existe une menace signifiante d'exposition aux risques environnementaux. Les FC doivent être capables d'identifier les dangers, de prendre des mesures qui minimisent l'exposition et de fournir des analyses complémentaires pour opérer efficacement dans ces théâtres. La possibilité de cas d'exposition à l'uranium appauvri durant les conflits de la guerre du Golfe et du Kosovo, a récemment soulevé des inquiétudes. Ceci a amené à établir chez les FC, des programmes d'essais biologiques d'uranium. À présent, deux cents membres actifs et à la retraite des FC ont soumis des échantillons d'urine pour les biotests d'uranium total et plus de quatre-vingt ont soumis des échantillons de cheveux pour les analyses de rapports isotopiques ($^{238}U/^{235}U$). Jusqu'à présent, les résultats ont été négatifs en ce qui concerne la présence d'uranium appauvri mais le problème de la sensibilité des méthodes analytiques employées a été soulevé.

Le but de cet exercice analytique était d'évaluer toutes les techniques analytiques disponibles ayant la capacité de mesurer les rapports isotopiques d'uranium ($^{238}U/^{235}U$) dans des concentrations en quantités infimes (sous-parties par billion) dans des liquides biologiques (p.ex: l'urine). On a choisi l'urine synthétique dans cette étude pour éliminer les inquiétudes au sujet des risques biologiques. Dans cette étude, on a opté pour les techniques comprenant la spectrométrie de masse à plasma inductif à haute résolution (ICP-SF-MS), la spectrométrie de masse quadripolaire à plasma inductif (ICP-Q-MS) la spectrométrie de masse à ionisation thermique (TIMS) et l'analyse par activation neutronique (NAA).

Résultats: Des ensembles de 12 échantillons (2 blancs et 10 dopés de quantités variées d'uranium naturel et appauvri) ont été préparés par le laboratoire hôte et envoyés à cinq laboratoires d'essais indépendants pour effectuer des biotests d'uranium total et de rapports isotopiques. Deux laboratoires de spectrométrie de masse à plasma inductif (à haute résolution et ICP-MS quadripolaire) ont soumis des mesures d'uranium total et de rapports isotopiques qui correspondaient aux valeurs des laboratoires hôtes. Les valeurs d'uranium total provenant de la TIMS et de l'NAA déviaient des valeurs des hôtes. Les deux techniques surestimaient l'uranium total à faible teneur et le sous-estimaient à teneur élevée. Les problèmes de précision des mesures annihilaient la haute précision des mesures de rapports isotopiques dans la TIMS. Les mesures partielles des rapports isotopes des ensembles provenant des NAA étaient les moins précises avec des rapports $^{238}U/^{235}U$ indiquant l'uranium enrichi ($^{235}U > 0.72\%$).

Signifiance: On a trouvé que l'analyse par activation neutronique (NAA) n'était pas adaptée aux biotests isotopiques et d'uranium total. Comparées à l'NAA, les techniques de spectrométrie de masse à plasma inductif, quadripolaire et à ionisation thermique (ICP-Q-MS, ICP-SF-MS et TIMS) étaient plus précises et avaient des limites plus basses de détection (pour les rapports isotopiques et d'uranium total).

Projets futurs: Il faudrait effectuer une seconde étude d'échantillons avec de l'urine réelle. L'uranium total dans >99% des échantillons d'urine analysés par le programme d'essais actuel des FC était inférieur à la concentration d'uranium (25 ng U/L d'urine synthétique) dans les blancs synthétiques. La seconde étude devrait inclure des échantillons d'urine naturelle contenant de l'uranium total allant de 1 ng U/L d'urine à 100 ng U/L d'urine. On a conclu que les trois techniques de SM (ICP-SF-MS, ICP-Q-MS et TIMS) étaient aptes à subir une étude longitudinale.

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Introduction

General

Following the Gulf War a number of military personnel suffered lingering health problems thought to be due to their wartime service. Although concern has been raised in the public about the role of depleted uranium in these illnesses, there is little support in the medical and scientific literature [1,2,3] for this assertion. Depleted uranium (DU), a byproduct of the uranium enrichment process, was used during the Gulf War [3,4,5] and later in the Kosovo conflict [6] because its properties greatly enhance both armor penetration and protection. Three NATO countries, the United States of America, Great Britain and France, have DU munitions in their military arsenals. American and British forces expended 300 tons of depleted uranium munitions during the 1990 Gulf War, while American forces used 11 tons in the Bosnia (1994-1995) and Kosovo (1999) conflicts. Although Canada had DU munitions in its military arsenal (Phalanx-Close-In-Weapons-Support System) aboard ships between 1990-1998, no Canadian DU was fired in combat.

A heightened awareness and concern over possible exposure to depleted uranium by Canadian Forces during Gulf War and Balkan operations has resulted in a number of testing programs within NATO [7,8], including a voluntary DU testing program for Canadian Forces personnel or former members [9]. The standard method for routine monitoring of occupationally exposed workers (e.g., mill workers, nuclear industry) is a urine collection and analysis. Since uranium is ubiquitous in nature, there will be background levels of natural uranium in urine samples collected from the general population and the presence of uranium in a urine sample does not is not necessarily indicate exposure to depleted uranium. Natural uranium contains two significant isotopes, ^{238}U and ^{235}U, present at 99.2745% and 0.7200%, respectively, while depleted uranium, the waste product of the enrichment process, typically contains ^{238}U and ^{235}U, at 99.745% and 0.250%, respectively [3]. Elevated levels of total uranium would be cause for concern from a heavy metal toxicity standpoint, but could not be attributed to DU exposure unless the ratio of ^{238}U to ^{235}U deviated from the ratio associated with naturally occurring uranium.

A number of analytical techniques, including neutron activation [10,11] and mass spectrometry [12,13,14], have been used for uranium determination with an increasing number of analysts making use of the speed, sensitivity and isotopic resolution (specificity) associated with the mass spectrometry techniques. Comparison of available analytical methods for the determination of total uranium and the ^{238}U to ^{235}U ratio in urine has not been performed frequently [15] and has not been attempted at the part-per-trillion background level normally observed in the general population [9]

An analytical capability for routine uranium determination does not currently exist within the Defence R&D Canada program, making identification of a reliable external source capable of providing this service on an on-going basis a priority. A host laboratory, skilled in the organization and preparation of analytical exercises [15] and samples was selected, and five laboratories were invited to analyse the host-provided urine samples using their analytical

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methods. Participating laboratories were provided with 12 synthetic urine samples (1 kg each, approximately 1 L in volume) containing varying amounts of natural and/or depleted uranium with no prior knowledge as to the urine spiking levels (if any). All laboratories were asked to provide their results for the determination of total uranium and the isotopic composition for inter-laboratory comparison by Defence R&D Canada (DRDC).

Host Laboratory

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Participating Laboratories

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Experimental

Host laboratory contract

The host laboratory prepared six identical sets of urine samples (1 kg each) containing natural and depleted uranium and distributed these sample sets to five participating laboratories. The spiked urine sample sets (12 samples/set) contained certified natural uranium and/or depleted uranium at the ng/kg level in a standard (synthetic) urine matrix. The host laboratory did not disclose the exact levels to anybody including DRDC employees and the Scientific Authority until after the analytical exercise.

The prepared samples were cross validated by NIST (US National Institute of Standards and Technology) to verify the presence of spiked natural uranium and/or depleted uranium in the sample sets.

Data obtained from each of the participating laboratories following analysis of the host laboratory prepared sample sets has been published anonymously (each laboratory referred to by letter only).

Host laboratory experimental

Sample preparation

The samples (Table 1) were prepared in accordance with the U.S. Department of Energy Laboratory Accreditation Program (DOELAP) In Vitro bioassay program.

Table 1. *Urine Recipe.*

Step	Component	Amount added
1	2% v/v nitric acid	~500 mL
2	Aliquot A	100 mL
3	Aliquot B	50 mL
4	Hippuric acid	0.63 g
5	Sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$)	0.071 g
6	2% v/v nitric acid	Dilute to 1000 gram total weight

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Shipping containers and sample shipment

IP2 shipping containers were utilized for the purposes of preparing these samples. Each bottle was pre-cleaned with 10% nitric acid to remove any leach-able uranium prior to use. The samples were shipped using FEDEX in accordance with international shipping regulations of hazardous materials (2% nitric acid).

Standard reference materials

Spiking materials were prepared using New Brunswick Laboratory (CRM U0002) for 0.02% depleted uranium and NIST Standard Reference Material 4321 for natural uranium. Samples were prepared using high purity acids and 18 MΩ de-ionized water. Total uranium content, of the prepared solutions, was confirmed, by NIST, using inductively coupled plasma atomic emission spectrometry (ICP-AES). The isotopic breakdown of CRM U0002 is provided in Table 2 and SRM 4321 is provided in Table 3.

Table 2. CRM U0002, depleted uranium isotopic composition.

	Atom %	Uncertainty
^{234}U	0.00016	0.00001
^{235}U	0.01755	0.00005
^{236}U	<0.00001	-
^{238}U	99.9823	0.0001

Table 3. SRM 4321, natural uranium isotopic composition.

	Atom %	Uncertainty
^{234}U	0.005254	0.000002
^{235}U	0.7199	0.0022
^{236}U	-	-
^{238}U	99.275	0.49

Verification of standard concentration by NIST

An aliquot of the standards used for completion of this work were supplied to NIST. Each pre-cleaned polyethylene bottle contained approximately 100 mL of standard. Additionally, ten 125 mL bottles containing 1 M HNO_3 (the same diluent used to prepare the standards) were provided. Based on these values, no significant difference at the 95% confidence level was observed between the expected and the determined values (Table 4).

Table 4. NIST analysis results.

	Expected	Uncertainty (%)	NIST value (ng/g)	% uncertainty	% Difference	# SD
Depleted uranium	497 2	0 3	494	0 22	0.6	1 74
Natural uranium	484 6	0 6	485	0 20	-0.08	0.13

Preparation of synthetic urine

The synthetic urine formulation used has been utilized by the US Department of Energy (DOE) Laboratory Accreditation Program (DOELAP) to conduct performance assessment of all laboratories performing urine bioassay analyses on DOE personnel. This formula contains the principal organic and inorganic interferences, urea being the principal component. Unlike actual human urine, the material has a consistent content and does not represent a biological hazard, an important factor when shipping materials internationally. The synthetic urine is stable for long periods of time, and because it is preserved in 2% nitric acid, is not subject to biological activity.

After cleaning, each bottle was provided a unique identifier and weighed. The samples were then prepared in accordance with the protocol outlined in Table 1. A 500 mL aliquot of 2% nitric acid was added to each bottle. The principal inorganic ingredients were then added from two stock solutions (Aliquot A per Table 5 and Aliquot B per Table 6). The inorganic components were prepared in two separate stock solutions due to the limitations on solubility posed by the $CaCl_2$ in aliquot B. The remaining two components were then added to the bottles to give the final DOELAP formula (Table 7).

The samples were then spiked by weight with an appropriate amount of spiking solution (see Table 8). The bottles were then brought to a final net solution weight of 1 000 g using 2% nitric acid, sealed, then enclosed in a heat sealed plastic bag for shipment.

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Table 5. *Aliquot A Formulation*

Step	Component	Amount added
1	2% v/v nitric acid	500 mL
2	Urea (CH_4N_2O)	160 00 g
3	Sodium sulfate (Na_2SO_4)	38 24 g
4	Potassium chloride (KCl)	34 30 g
5	Sodium chloride (NaCl)	23.20 g
6	Creatinine ($C_4H_7N_3O$)	11.00 g
7	Ammonium chloride (NH_4Cl)	10.60 g
8	Citric acid ($C_6H_8O_7$)	5 40 g
9	Glucose ($C_6H_{12}O_6$)	4.80 g
10	Magnesium sulfate ($MgSO_4$)	4 60g
11	Pepsin	0.29 g
12	Oxalic acid ($C_2H_2O_4$)	0.28 g
13	Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$)	27 30 g
14	Lactic acid ($C_3H_6O_3$)	0 94 g
15	2% v/v nitric acid	Dilute to 1000 mL total volume

Table 6. *Aliquot B Formulation.*

Step	Component	Amount added
1	2% v/v nitric acid	500 mL
2	Calcium chloride ($CaCl_2 \cdot 2H_2O$)	12.6 g
3	2% v/v nitric acid	Dilute to 1000 mL total volume

Table 7. *Final urine composition as prescribed by DOELAP.*

Component	g/kg
Urea (CH_4N_2O)	16.00
Sodium sulfate ($Na_2SO_4 \cdot H_2O$)	4.31
Potassium chloride (KCl)	3.43
Sodium chloride (NaCl)	2.32
Creatinine ($C_4H_7N_3O$)	1.10
Ammonium chloride (NH_4Cl)	1.06
Hippuric acid ($C_9H_9NO_3$)	0.63
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	0.63
Citric acid ($C_6H_8O_7$)	0.54
Glucose ($C_6H_{12}O_6$) (Dextrose)	0.48
Magnesium sulfate ($MgSO_4$)	0.46
Sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$)	0.071
Pepsin	0.029
Oxalic acid ($C_2H_2O_4$)	0.02
Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$)	2.73
Lactic acid ($C_3H_6O_3$)	0.094
2% v/v nitric acid	966

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Table 8. Spiking protocol using natural and depleted uranium standards.

Sample Number	Expected Background uranium	Natural uranium spike (ng)	Depleted uranium spike (ng)	Total uranium content (ng)	Final $^{235}U/^{238}U$ ratio (%)
1	25.2 ± 2.5	177.0	45.2	247 ± 21	0.595%
2	25.2 ± 2.5	0.0	0.0	25.2 ± 2.5	0.725%
3	25.2 ± 2.5	236.4	161.4	423 ± 25	0.454%
4	25.2 ± 2.5	394.2	150.5	570 ± 32	0.537%
5	25.2 ± 2.5	196.2	101.2	323 ± 23	0.502%
6	25.2 ± 2.5	63.8	45.5	134 ± 13	0.485%
7	25.2 ± 2.5	39.3	10.1	75 ± 10	0.629%
8	25.2 ± 2.5	9.7	20.1	55 ± 5.6	0.466%
9	25.2 ± 2.5	49.4	19.9	95 ± 12	0.575%
10	25.2 ± 2.5	643.6	101.2	770 ± 41	0.632%
11	25.2 ± 2.5	0.0	0.0	25.2 ± 2.5	0.725%
12	25.2 ± 2.5	147.2	25.2	198 ± 20	0.633%

Participating laboratories contract

Participating laboratories were provided with urine samples (1 kg each, approximately 1 L in volume) containing varying amounts of natural and/or depleted uranium. Samples were prepared and distributed by a host laboratory chosen by DRDC. The participating laboratories had no prior knowledge as to the urine spiking levels (if any) and were asked to provide their results for determination of total uranium and its isotopic composition in urine for inter-laboratory comparison.

Each participating laboratory used "in-house" analytical methods (sample handling and analysis) for the detection and determination of total uranium and its isotopic composition in the provided urine samples. The laboratory reported the total uranium present in each urine sample as ng/kg and the $^{238}U/^{235}U$ isotopic ratio of the urine sample. The laboratory performed 3 to 5 measurements on each urine sample, reporting the mean value for each urine sample and the percent standard deviation (2 s) for the mean value. A Figure illustrating typical collected data (if the method permits) was included.

A sample (or method) detection limit (ng/kg) for ^{238}U and ^{235}U in urine, based on a S/N ratio of 5:1, was estimated based on the least concentrated spiked urine sample(s) analyzed.

Laboratory A experimental

Instrumentation

The sector field ICP-MS instrument (ICP-SF-MS) used was the ELEMENT (Finnigan MAT, Bremen, Germany) equipped with an ASX 500 sample changer (CETAC Technologies Inc., Omaha, USA). The device was operated in low-resolution mode (LRM, $m/\Delta m$ about 400). Details on instrumental operating conditions and measuring parameters are given in Tables 9 and 10.

***Table 9.** Instrumental operating conditions for the ICP-SF-MS.*

Rf power/W	1450
Sample uptake rate/ml min^{-1}	0.4
Gas flow rates/l min^{-1}	
Coolant	14
Auxiliary	0.8
Nebulizer	0.95
Ion sampling depth/mm	11
Ion lens settings	Adjusted to obtain maximum signal intensity
Torch	Fassel torch, 1.5 mm id
Nebulizer	MicroMist
Spray chamber	Scott type (double-pass)
Sample cone	nickel, 1.1 mm orifice diameter
Skimmer	nickel, 0.8 mm orifice diameter

***Table 10.** Measurement parameters for the ICP-SF-MS.*

Uranium concentrations	
Isotopes	^{115}In, ^{169}Tm, ^{235}U, ^{238}U, ^{238}U^{16}O
Acquisition mode	E-scan
No. of scans	75
Acquisition window/%*	10
Search window/%*	10
Integration window/%*	10
Dwell time per sample/ms	10 for ^{115}In and ^{169}Tm; 50 for other isotopes
No. of samples per nuclide	60
Isotopic ratios	
Isotopes	^{235}U, ^{238}U
Acquisition mode	E-scan
No. of scans	450
Acquisition window/%*	5
Search window/%*	5
Integration window/%*	5
Dwell time per sample/ms	50 for ^{238}U, 500 for ^{235}U
No. of samples per nuclide	20

* Percent of peak width

Chemicals and reagents

All calibration and internal standard solutions used were prepared by diluting 1 g/L single-element standard solutions (SPEX Plasma Standards, Edison, NJ, USA). Analytical grade nitric acid (Merck, Darmstadt, Germany) was used after additional purification by sub-boiling distillation in a quartz still. For dilution of urine samples, blanks and standards Milli-Q water (Millipore Milli-Q, Bedford, USA) additionally purified by sub-boiling distillation in a Teflon still (Savillex Corp., Minnetonka, Minnesota, USA), was used.

Sample preparation

Urine samples were stored in a refrigerator prior to analysis. Neither uranium pre-concentrations nor matrix separation was performed. For determination of total uranium content, a 1 mL aliquot of urine was transferred into a disposable 10 mL Nalgene polypropylene autosampler tube and made up to 10 mL with 0.14 M HNO_3 in ultrapure water. Four to five replicate dilutions were prepared for each sample. In order to test recovery of uranium from urine matrix, aliquots of one urine sample (D2) were spiked to 100 ng/L, 200 ng/L and 300 ng/L. For uranium isotope ratio measurements, a 2 mL aliquot of urine was transferred into a disposable 10 mL Nalgene polypropylene autosampler tube and made up to 10 mL with 0.14 M HNO_3 in ultrapure water. A set of synthetic blanks (0.14 M HNO_3) and calibration standards (in the range 10 ng U/L - 1000 ng U/L) was prepared as well. The resulting solutions were spiked to 20 µg/L of In and to 10 µg/L of Tm as internal standards. Prior to use, plastic labware was thoroughly cleaned in a sequence with detergent, water, mixture of nitric (1.4 M) and hydrochloric (1.1 M) acids (1:1 v/v, Merck, analytical grade) followed by soaking in distilled nitric acid (0.7 M) and a final rinse with de-ionized water.

Measurement sequence and data handling

Determination of total uranium content was performed during two separate analysis sequences: first using In as an internal standard (two replicate dilutions of each urine samples), second using Tm as an internal standard (two to three replicate dilutions of each urine samples). During each sequence, solutions were analysed in the following order: calibration blank, set of calibration standards, 2-3 wash blanks, diluted urine samples, blank and set of quality control standards.

The sum of intensities for ^{235}U and ^{238}U were corrected for variation in plasma using internal standard intensities. Instrumental response was calculated from corrected intensities for calibration standards. Uranium isotope ratio measurements were corrected for mass bias using a mass discrimination factor obtained from measured ratios for a uranium standard with natural isotopic composition.

Laboratory B experimental

Instrumentation

The quadrupole ICP-MS instrument (ICP-Q-MS) used was the Perkin Elmer-Sciex Elan 6000. Details on instrumental operating conditions and measuring parameters are given in Tables 11 and 12.

Table 11. *Instrumental operating conditions for the ICP-Q-MS.*

Rf power/W	1200-1350
Sample uptake rate/ml min^{-1}	3
Gas flow rates/L min^{-1}	
Plasma	
Auxiliary	
Nebulizer	0.98-1.08
Ion lens settings/V	6.5-8.5
Detector	
Torch	Quartz
Nebulizer	Conikal Nebulizer-STF (concentric)
Spray chamber	Tracey Spray Chamber

Table 12. *Measurement parameters for the ICP-Q-MS.*

Channels per peak	
Scan mode	
Points per peak	
Dwell time/ms	200
Sweeps/reading	30
Reading/replicate	1
Number of replicates	5
Read delay/s	50

Sample preparation and analysis

Total uranium and the $^{238}U/^{235}U$ isotopic ratios in the synthetic urine samples was analysed according to the test laboratories QOP procedure for using the Elan ICP-MS to determine total and isotopic ratio of uranium in urine samples [16,17]. Re-validation of the procedures occurs yearly according to QCP-validate.

Laboratory C experimental

Sample preparation and analysis

All sample processing and ion exchange chemistry was completed in a class 100 clean laboratory.

Approximately 500 grams of each test sample was accurately weighed in 1000 mL Teflon lined beakers for isotopic composition determination. The samples were then evaporated to dryness. Each sample residue was dissolved in 5 mL of 16M 2 bottle (2B) distilled nitric acid and then evaporated to near dryness. This step was repeated several times to ensure

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decomposition of any organic material present in the test samples. All twelve samples were evaporated one final time to dryness and the residues dissolved in 3M 2B nitric acid prior to ion exchange chemistry.

Approximately 75 grams of each test sample was accurately weighed in 100 mL Teflon lined beakers for isotopic dilution determination. The samples were then evaporated to dryness. Each sample residue was dissolved in 5 mL of 16M 2B distilled nitric acid and then evaporated to near dryness. This step was repeated several times to ensure decomposition of any organic material present in the test samples. An accurately weighed amount of a ^{235}U spike was added to each of the isotopic dilution fractions. All twelve samples were evaporated one final time to dryness and the residues dissolved in 3M 2B nitric acid prior to ion exchange chemistry.

Ion exchange chemistry was carried out using an element specific exchange resin, UTEVA made by EICHROM Industries, Ltd. The uranium was separated and collected, for both isotopic composition and isotopic dilution analysis, by standard separation techniques for the UTEVA resin. The resins were calibrated using ICP-Q-MS to precisely determine uranium separation. All acids and water used during sample digestion and ion exchange separation were double distilled using a double Teflon bottle distillation setup.

Instrumentation

Uranium sample loading for mass spectrometric analysis was performed in a class 100 clean box. All acids and water used during sample digestion and ion exchange separation were double distilled using a double Teflon bottle distillation setup. The uranium fractions were loaded with phosphoric acid and gel onto separate outgassed rhenium ribbons. The isotopic compositions were measured on a multi-collector Finnegan MAT 262 thermal ionization mass spectrometer operating in peak jumping mode using the secondary electron multiplier (SEM) detector and ion counting system. The ^{235}U spiked samples were analysed the same procedure, in order to determine the spiked isotope ratios and to calculate the concentration of uranium in the samples.

The uranium blank for the laboratory was determined by analysing a blank sample that was processed in the same manner as the test samples.

Laboratory D experimental

Sample preparation and analysis

Uranium was collected from 700 mL of each sample as follows: calcium nitrate and nitric acid were added to each sample and the sample was heated to just below boiling for about three hours and was then allowed to cool. Sodium phosphate was added and concentrated ammonium hydroxide was added to obtain a pH of 9 and to precipitate calcium phosphate. The precipitate was collected and entrained organic matter was oxidized with hydrogen peroxide. The precipitate was dissolved in dilute hydrochloric acid and uranium present was reduced with titanium chloride solution. Hydrofluoric acid was then added to give a calcium fluoride precipitate. This precipitate was dried and taken for irradiation. The yield of this process was estimated by analyzing spiked local urine samples.

Instrumentation

Samples prepared for analysis were sent to the McMaster University Nuclear Reactor (Hamilton, ON, Canada) for neutron activation analysis.

Conventional neutron activation analysis was carried out as follows: samples, blanks and standards were irradiated in an epithermal flux of about 10^{11} neutrons/cm^{2}s for one hour. After about five days, each sample was counted for four hours on a germanium detector. The concentration of ^{238}U was computed from the gamma-ray spectra collected.

Delayed neutron counting was carried out as follows: samples, blanks and standards were irradiated at a flux of about 10^{12} neutrons/cm^{2}s for sixty seconds, allowed to decay for ten seconds and counted in a neutron detector for sixty seconds. The concentration of ^{235}U was computed from the data collected.

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Results and discussion

Total Uranium

The total uranium results, as reported by the four testing laboratories, have been recorded in Table 13. With the exception of Lab C, all other testing laboratories report the standard deviation (2 sigma) on their measurements. Samples #2 and #11 are blank samples, which contain no added natural or depleted uranium standards. The uranium present in these blanks arises from uranium impurities in the synthetic urine samples. The blank values reported by Lab A and Lab B, plus those reported in a previous United States Department of Energy (USDOE) inter-laboratory comparison [15] were used to set the background uranium concentration in the synthetic urine samples at 25.2 ± 2.5 ng U/L synthetic urine. This background value was used to set the concentration of uranium and the isotope ratio ($^{238}U/^{235}U$) in the spiked synthetic urine samples.

Table 13. *Total Uranium determined by participating laboratories.*

Sample Number	Total Uranium (ng kg^{-1})[a]				
	Host Lab	Lab A[b] (n=5)	Lab B[c] (n=5)	Lab C[d]	Lab D[e]
1	247 ± 21	251 ± 6	256 ± 26	221.9	137 ± 22
2	25.2 ± 2.5	24 1 ± 1.4	25 ± 2.4	37.4	32 ± 19
3	423 ± 25	430 ± 14	444 ± 20	358.3	367 ± 55
4	570 ± 32	564 ± 38	584 ± 50	470.4	354 ± 57
5	323 ± 23	331 ± 16	333 ± 18	281 2	242 ± 51
6	134 ± 13	132 ± 16	136 ± 8	127 2	93 ± 38
7	75 ± 10	75.7 ± 3 6	74 4 ± 7 4	77.3	44 ± 33
8	55 ± 5 6	57 3 ± 4.6	54.1 ± 6 8	61 2	46 ± 32
9	95 ± 12	96 6 ± 6.0	94.6 ± 6 0	97.2	70 ± 35
10	770 ± 41	764 ± 34	769 ± 66	640 8	675 ± 81
11	25.2 ± 2.5	26 6 ± 0 6	20.0 ± 5 8	38 4	27 ± 25
12	198 ± 20	202 ± 12	206 ± 40	178 3	176 ± 35

[a] Mean ± 2 standard deviations
[b] Sector field ICP-MS (Finnegan MAT ELEMENT).
[c] Quadrupole ICP-MS (Perkin Elmer-Sciex Elan 6000)
[d] thermal ionization mass spectrometry (Finnegan MAT 262)
[e] instrumental and delayed neutron activation

The results from Table 13 have also been plotted in Figure 1 where the total uranium calculated by the host lab has been plotted against the values determined by the testing labs. The results from regression analysis on the four sets of data (host lab vs. lab A, host lab vs.

lab B, host lab vs. lab C and host lab vs. lab D) are listed in Table 14. The regression results for lab A (ICP-SF-MS), lab B (ICP-Q-MS) and lab C (TIMS) show excellent agreement between individual values and the fitted lines (correlation coefficients >0.999), while the results for lab D (INAA) exhibit greater scatter around the line of best fit (correlation coefficient ~ 0.95). The results from lab A (ICP-SF-MS) and lab B (ICP-Q-MS) are in good agreement with the host lab values with the fitted lines overlapping the 1:1 line. The results from lab C (TIMS) and lab D (INAA) deviate significantly from the 1:1 line, and the fitted lines have slopes around 0.80 and intercepts that deviate significantly from zero.

Table 14. *Regression analysis of testing laboratories total uranium analysis of the 12 synthetic urine samples.*

	Intercept (ng/kg)	Slope	Correlation Coefficient
Lab A[a]	2.76	0.993	0.9997
Lab B[b]	0.881	1.02	0.9992
Lab C[c]	18.7	0.804	0.9997
Lab D[d]	-8.00	0.802	0.9544

[a] Sector field ICP-MS (Finnegan MAT ELEMENT).
[b] Quadrupole ICP-MS (Perkin Elmer-Sciex Elan 6000)
[c] thermal ionization mass spectrometry (Finnegan MAT 262)
[d] instrumental and delayed neutron activation

Uranium Isotope Ratio ($^{238}U/^{235}U$)

Table 15 contains host lab values for the isotope ratio ($^{238}U/^{235}U$) along with the values reported by the four testing laboratories. The neutron activation lab (lab D) has provided an incomplete set of isotopic ratios and will not be considered in the subsequent analysis of these results. The host lab isotope ratio ($^{238}U/^{235}U$) versus test lab isotope ratio ($^{238}U/^{235}U$) for total uranium concentrations between 25 ng/kg and 100 ng/kg (5 samples), 100 ng/kg and 350 ng/kg (four samples), and >350 ng/kg (3 samples) have been plotted in Figures 2-4, respectively.

It is not unexpected that the best agreement between host and the three MS laboratories is seen in the sample #10 ($^{238}U/^{235}U = 158$), which has the highest concentration of uranium (Figure 4). The largest variance is observed for sample #8, which is the lowest spiked sample with one of the highest percentages of depleted uranium (~49%). The greatest deviation from the host values (for this and other samples) is observed for the TIMS results. Although the TIMS derived isotope ratios have the smallest standard deviations (<0.4% RSD), from the point of view of accuracy they are consistently off the values reported by the host laboratory.

Within the error associated with their measurements, the ICP-SF-MS and ICP-Q-MS laboratories report isotope ratios that are consistent with the values reported by the host laboratory. The sector field ICP-MS laboratory consistently reported RSD (2σ) values

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smaller than the ICP-Q-MS laboratory. This is readily observable in Figure 2, where host versus test laboratory results are plotted for those samples with >100 ng U/kg synthetic urine.

Table 15. $^{238}U/^{235}U$ *isotopic ratio determined by participating laboratories.*

Sample Number	Total Uranium (ng kg^{-1})[a]	$^{238}U/^{235}U$ isotopic ratio[b]				
		Host Lab	Lab A[c] (n=3)	Lab B[d] (n=5)	Lab C[e] (n=2-4)	Lab D[f] (n=)
1	247 ± 21	168 ±2	167 ± 1	167 ± 10	170 5 ± 0 1	159 ± 222
2	25.2 ± 2 5	138 ±10	133 ± 8	138 ± 8	137 9 ± 0 1	
3	423 ± 25	220 ±3	216 ± 5	220 ± 8	213 4 ± 0 2	196 ± 131
4	570 ± 32	186 ±2	183 ± 2	187 ± 4	183 0 ± 0 2	90 ± 32
5	323 ± 23	199 ±3	194 ± 3	198 ± 6	192 4 ± 0 4	137 ± 96
6	134 ± 13	206 ±4	205 ± 1	199 ± 6	194 3 ± 0 2	100 ± 130
7	75 ± 10	159 ±4	158 ± 5	157 ± 14	153 9 ± 0 5	
8	55 ± 5 6	215 ±9	218 ± 8	205 ± 20	186 1 ± 0 3	
9	95 ± 12	174 ±4	174 ± 2	168 ± 14	166 5 ± 0 3	
10	770 ± 41	158 ±2	158 ± 2	157 ± 2	158.3 ± 0 3	132 ± 40
11	25 2 ± 2 5	138 ±10	136 ± 11	129 ± 10	138 5 ± 0 1	
12	198 ± 20	158 ±2	156 ± 5	160 ± 4	156 4 ± 0 1	167 ± 183

[a] As determined by host laboratory
[b] Mean ± 2 standard deviations.
[c] Sector field ICP-MS (Finnegan MAT ELEMENT).
[d] Quadrupole ICP-MS (Perkin Elmer-Sciex Elan 6000)
[e] thermal ionization mass spectrometry (Finnegan MAT 262)
[f] instrumental and delayed neutron activation

Fraction Depleted Uranium in Samples

The $^{238}U/^{235}U$ isotope ratios (Table 15) were used to calculate the fraction of depleted uranium in the set of samples (Table 16). For this report, DU has 0.2% (by mass) ^{235}U. Samples #2 and #11 are the blank samples and only contain natural uranium. Within the ten spiked samples, the percent DU varies from 17.2% to 51.5% (host laboratory values). From Table 16, it can be observed that all three MS techniques are generally within 5% (excluding #6 and #8 for TIMS) of the value reported by the host laboratory.

Table 16. Fraction depleted uranium determined from the $^{235}U/^{238}U$ isotopic ratios provided by participating laboratories.

Sample Number	^{238}U (ng kg^{-1})[a]	Fraction Depleted Uranium[b]				
		Host Lab	Lab A[c]	Lab B[d]	Lab C[e]	Lab D[f]
1	247 ± 21	.247	241	240	0 263	
2	25.2 ± 2 5	0	0	0	0	
3	423 ± 25	515	501	514	0.488	
4	570 ± 32	357	341	.362	.339	
5	323 ± 23	424	401	418	390	
6	134 ± 13	457	.451	423	400	
7	75 ± 10	183	.173	168	.143	
8	55 ± 5 6	494	506	.453	357	
9	95 ± 12	284	.285	247	237	
10	770 ± 41	.178	173	168	178	
11	25.2 ± 2.5	0	0	0	0	
12	198 ± 20	172	.159	.190	0.163	

[a] As determined by host laboratory.
[b] Based on 0.2% ^{235}U isotopic abundance in depleted uranium
[c] Sector field ICP-MS (Finnegan MAT ELEMENT)
[d] Quadrupole ICP-MS (Perkin Elmer-Sciex Elan 6000)
[e] thermal ionization mass spectrometry (Finnegan MAT 262)
[f] instrumental and delayed neutron activation

Instrument detection limits

As part of the contract, the testing laboratories were required to calculate detection limits for total and isotope ratio assays. The results are presented in Table 17. The relative sensitivity of the four techniques is TIMS > ICP-SF-MS > ICP-Q-MS > NAA. The results are in-line with the information available in the literature [19].

Table 17. Total uranium and isotopic ($^{238}U/^{235}U$) ratio detection limits.

Participating Lab	U_{total} (ng kg^{-1})[a]	$^{238}U/^{235}U$ (ng kg^{-1})[a,b]
A[c]	0 025	3.5
B[d]	0 1	13 9
C[e]	0 12 picograms	16 5 picograms
D[f]	50	50

[a] based on ^{238}U concentration
[b] based on $^{238}U/^{235}U$ of 137 88
[c] Sector field ICP-MS (Finnegan MAT ELEMENT)
[d] Quadrupole ICP-MS (Perkin Elmer-Sciex Elan 6000)
[e] thermal ionization mass spectrometry (Finnegan MAT 262)
[f] instrumental and delayed neutron activation

Isobaric Interference in MS Analyses

A concern with ICP-MS is the presence of isobaric interference. An example would be the interference of the uranium-238 hydride ($^{238}U^1H^+$) species with the measurement of the plutonium-239 (^{239}Pu) isotope [18]. The formation constant for $^{238}U^1H^+$, which depends on the ICP torch conditions and the choice of nebulizer, is reported to range from 10^{-4} to 10^{-5} ($^{238}U^1H^+/^{238}U$) [18] The 230-240 Da mass spectrum of sample #10 (provided by the ICP-SF-MS laboratory) has a weak peak (~5 cps) characteristic of the $^{238}U^1H^+$ adduct (the formation constant is ~5 X 10^{-5}). It has been reported that some ICP-SF-MS measurements of the ^{238}U concentration in urine samples were affected by isobaric interference [8]. Since the formation of the uranium hydride is independent of the isotopic form of uranium, it is to be expected that a $^{235}U^1H^+$ adduct will also be present in the mass spectrum and that it will complicate quantitative and qualitative determination of the ^{236}U isotope.

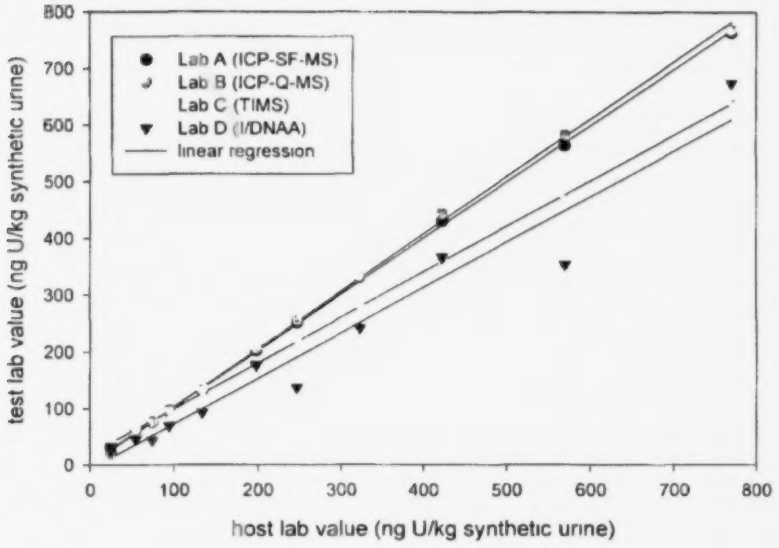

Figure 1. *Total uranium determined by participating laboratories graph of total uranium versus known value (as determined by the host laboratory)*

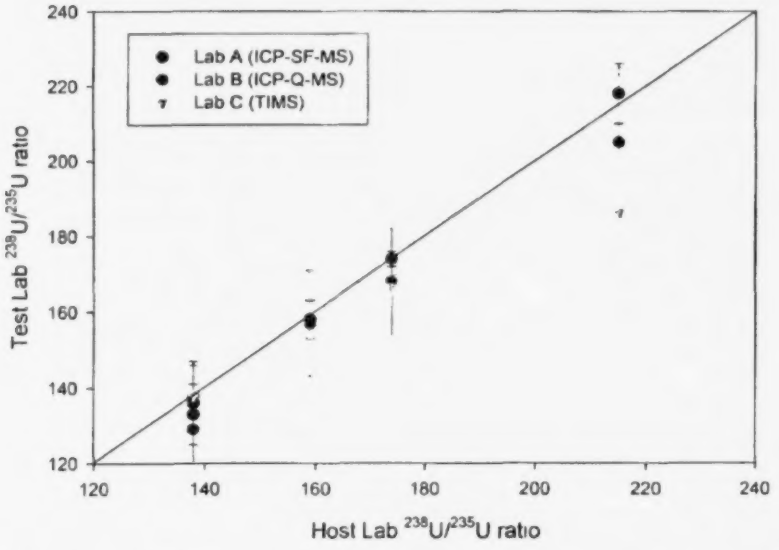

Figure 2. *$^{238}U/^{235}U$ ratios determined by participating laboratories (for samples containing 25 ng kg^{-1} to 100 ng kg^{-1} of total uranium)*

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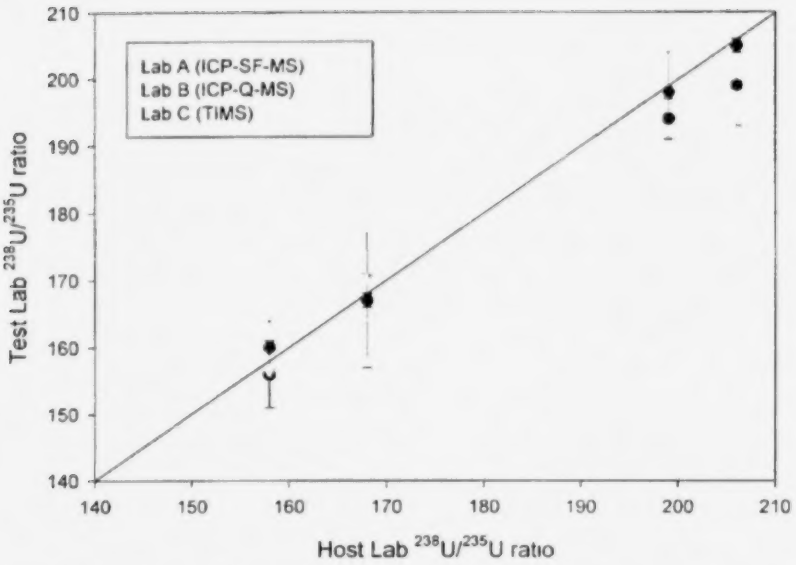

Figure 3. *$^{238}U/^{235}U$ ratios determined by participating laboratories (for samples containing 100 ng kg^{-1} to 350 ng kg^{-1} of total uranium)*

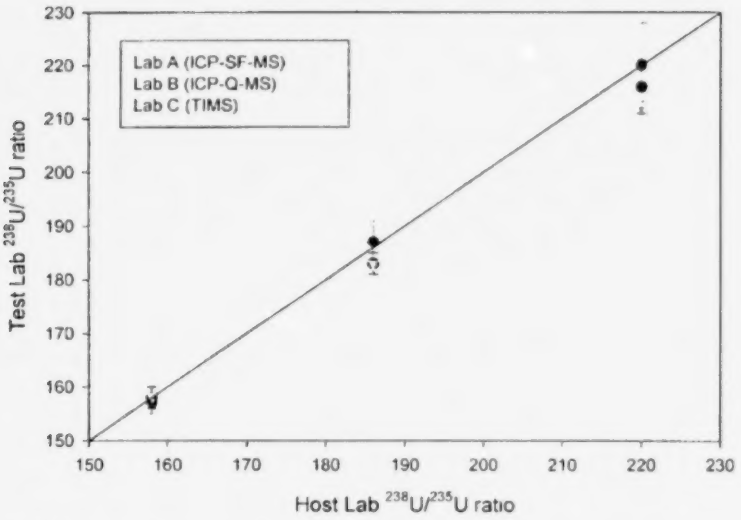

Figure 4. *$^{238}U/^{235}U$ ratios determined by participating laboratories (for samples containing >350 ng kg^{-1} of total uranium).*

Conclusions

The four analytical procedures were ranked ICP-SF-MS (1), ICP-Q-MS (2), TIMS (3) and NAA (4). The ranking is based on a technique's abilities to accurately reproduce both the concentration of total uranium and the isotope ratio ($^{238}U/^{235}U$). Neutron activation analysis (NAA) was incapable of accurately measuring both the total uranium and the $^{238}U/^{235}U$ ratio. Potential calibration problem(s) in the total uranium assay and inaccuracy in the isotope assay placed TIMS behind the two ICP-MS techniques in the overall ranking. ICP-SF-MS ranks higher than ICP-Q-MS because of lower instrument detection limits and smaller standard deviations on reported numbers.

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An analytical exercise was initiated in order to determine those analytical procedures with the capacity to measure uranium isotope ratios ($^{238}U/^{235}U$) in urine samples containing less that 1 µg uranium /L urine. A host laboratory was tasked with the preparation of six sets (12 samples per set) of synthetic urine samples spiked with varying amounts of natural and depleted (0.2% ^{235}U) uranium. The sets of samples contained total uranium in the range 25 ng U/L urine to 770 ng U/L urine, with isotope ratios ($^{238}U/^{235}U$) from 137.9 (natural uranium) to 215 (~50% depleted uranium). Sets of samples were shipped to five testing laboratories (four Canadian and one European) for total and isotopic assay. The techniques employed in the analyses included sector field inductively coupled plasma mass spectrometry (ICP-SF-MS), quadrupole inductively coupled plasma mass spectrometry (ICP-Q-MS), thermal ionization mass spectrometry (TIMS) and neutron activation analysis (NAA). Full results were obtained from three testing labs (ICP-SF-MS, ICP-Q-MS and TIMS). Their results, plus partial results from the NAA lab, have been included in this report. Total uranium and isotope ratio results obtained from ICP-SF-MS and ICP-Q-MS were in good agreement with the host lab values. Neutron activation analysis and TIMS reported total uranium concentrations that differed from the host lab. An incomplete set of isotopic ratios was obtained from the NAA lab with some results reporting enriched uranium ($\%^{235}U > 0.7$). Based on the reported results, the four analytical procedures were ranked: ICP-SF-MS (1), ICP-Q-MS (2), TIMS (3) and NAA (4).

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Uranium
Depleted uranium
Mass spectrometry
Neutron activation
Urine
Analytical exercise

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